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Chlorides removal and control through water-washing process on MSWI fly ash

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Abstract

Wet pretreatment is widely employed as the most economic method to treat municipal solid waste incineration (MSWI) fly ash. Meanwhile, much wastewater containing high concentration of chlorides generated during the wet process if the liquid-solid weight ratio was not appropriate. So measures were taken to control the dissolving amounts of calcium chlorides which contribute to the further reuse as basis with cement kiln and remove more chlorides like sodium chloride (NaCl), potassium chloride (KCl) and so on which produce negative impact. In laboratory experiments, the water-washing process was applied to study the typical MSWI fly ash and investigate the optimal parameters. First, multi-step water-washing process was carried out and key parameters influencing the removal rate of chlorides were determined. Then, cyclic water-washing process was conducted to overcome defects on the basis of the former. In this experiment, calcium hydroxide as a cheap and easily got chemical was added to affect the ionic equilibrium and solubility equilibrium associated with calcium. When compared with the original fly ash, calcium chlorides remained in the treated fly ash won't be a huge loss while other chlorides are greatly reduced. Combined with the demand for raw materials of low chlorine in cement production, it's potential for MSWI fly ash after wet treatment to be applied in cement kiln when this ash in the cement kiln is at a lower rate of substitution.

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1. Introduction

With the continuous development of urbanization and enhancement of people's living standard, domestic municipal waste output is growing at an annual rate of 8% to 10%[1]. Basic methods of disposing municipal solid waste are consisted of landfill, incineration and composting in which incineration is widely used because it fulfills the requirement of waste disposal in harmlessness, reduction and reuse. However, waste incineration technology also has its shortcomings and the main residue of MSWI fly ash enriches a higher concentration of heavy metals and other hazardous substances like dioxins and furans. Additionally, this fly ash is classified as hazardous waste by "National Catalogue of Hazardous Wastes" because of its high leaching concentration of heavy metals and toxic equivalent of dioxins.

Currently, effective treatments for MSWI fly ash are mainly cement solidification[2], heat treatment[3], chemical stabilization[4] and resourceful utilization[5]. Considering the similarity of main chemical composition between MSWI fly ash and raw materials such as coal ash, slag and so on which are widely used in cement industry, this MSWI fly ash could be employed to replace part of raw materials in cement and concrete manufacturing[6, 7]. More importantly, heavy metals, dioxin, furan and other toxic substances could be stabilized or completely decomposed in the unique environment of high temperature which is up to 1450℃ and alkaline atmosphere in cement kiln[8]. However, there will be a lot of volatile containing high concentration of metal chlorides from fly ash due to the high temperature which present great threat to the normal operation of the kiln system and even the quality of products from the cement kiln[9].Obviously, the chlorides in the MWSI fly ash produced during incineration are the main consideration of its comprehensive utilization.

Therefore, chlorides must be removed and controlled before the MSWI fly ash is utilized for resource. A lot of soluble chlorides such as NaCl, KCl, $CaCl_2$ and $CaCl_2$•$Ca(OH)_2$•H_2O were removed after the process of water-washing and the results of energy spectrum analysis also demonstrated that the loss of a large number of chlorides, which proved that it was a good way for water-washing to remove the high concentration of chlorides in MSWI fly ash[10]. Other scholars conducted washing experiments for MSWI fly ash to remove chlorides and a method of taking advantages of solubility difference in ethanol to recover these chlorides was developed which meant that large quantities of chlorides in MSWI fly ash could be removed[11].

However, much wastewater containing high concentration of chlorides and heavy metals generated after experiments especially if the goal of the trial is to remove all chlorides by washing singly. So the research in this paper is to determine key parameters which help to remove and control chlorides. And in order to improve the recycling rate of water resources, cyclic washing process was developed. Additionally, calcium hydroxide was added to stop the calcium components from losing severely. This technology will be a supplement to the washing treatment for the MSWI fly ash.

2. Materials and methods

2.1. Materials

The MSWI fly ash for this research, which appears to be grey colour, comes from Beijing municipal solid waste incineration plants in China. About 80% of the particle size is below 100μm. Bulk density of the fly ash is around $0.73 g/cm^3$. Moisture content is about 4.22% and pH for the filtrate of the fly ash is about 12.72. Fly ash samples after grinding sieved through a 150-mesh standard sieve, then it was dried under 105℃ after 8h to constant weight. Finally it was stored for experiment in brown glass bottle.

2.2. Methods

Multi-step water-washing process and cyclic water-washing process were conducted sequentially to determine the optimal parameters for the removal and control of chlorides in MSWI fly ash. Orthogonal Test of $L_{16}(4^5)$ is employed during former experiment to study the parameters like liquid-solid ratio (L), temperature (T), washing time (W), vibration rate (V) and frequency of dealing (D), influencing the removal rate of chlorides (F_1) and soluble solids (F_2). The water-washing experiments were carried on with deionized water as the extracting agent in water bath vibration tank. During the latter experiment, one batch was consisted of twice washing process and three batches constituted the entire cycle in which the washing water for first batch would went for the second and the third. After the washing process, the solid and liquid mixture was filtered by vacuum filtration and the filtrate was used to calculate the leaching amount of chlorine. At the same time, the filtration cake was dried to constant weight and weighed. In cyclic water-washing process, the core cycle was consisted of three batches of same washing experiments which were aimed to reduce and reuse the deionized water. Finally, in order to reduce the dissolution of calcium compounds, saturated calcium hydroxide solution was prepared to replace the deionized water for washing when the experimental conditions were set at the optimal parameters of multi-step water-washing process. Flow charts for two different processes above are shown in Fig. 1.

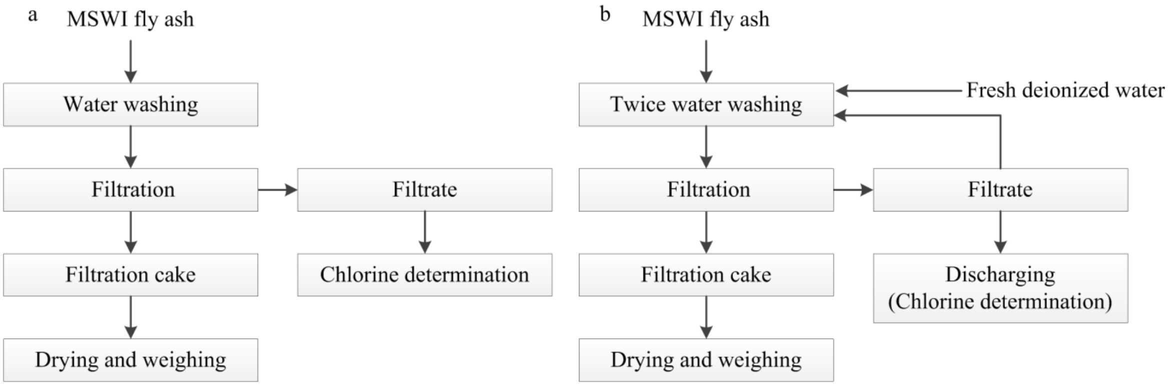

Fig. 1. (a) Flow charts for multi-step washing process; (b) Flow charts for cyclic washing process

2.3. Analysis

The filtration cake was dried completely in vacuum drying oven and weighed accurately by electronic balance. The leaching amount of chlorine in the filtrates was calculated according to Chinese National Standard GB 11896-89. Chemical composition of sample was determined by X-ray fluorescence (XRF).

3. Results and analysis

3.1. Sample characterization

Due to the diversity of municipal solid waste and special treatment of flu gas from municipal solid waste incineration plants, MSWI fly ash is actually a mixture of different compounds. Table 1 shows the chemical composition of a fly ash sample. The fly ash as the materials is rich in chloride compounds ($NaCl$, KCl, $CaCl_2$) and calcium compounds (CaO, $CaCl_2$). The minor components in the fly ash were heavy metal compounds such as PbO which would form the potential leaching problem of heavy metal elements. Because of the existence of strong alkaline oxide (CaO), the solution was strongly alkaline in which the heavy metal elements would form hydroxides precipitations. Paradoxically, calcium, silicon and other elements could be raw materials added during cement production while high level of chloride in MSWI fly ash affected the normal operation of the cement kiln seriously when most calcium compounds which are soluble dissolved into water solution during washing experiments.

Table 1. Chemical composition of MSWI fly ash (%).

Composition	MSWI fly ash
CaO	23.12
SiO_2	18.64
$CaCl_2$	11.03
MgO	3.78
K_2O	3.04
Al_2O_3	9.86
Fe_2O_3	5.45
Na_2O	2.33
P_2O_5	1.18
TiO_2	1.79
SO_3	17.50
PbO	0.25
Trace components	2.03

3.2. Effects of multi-step water-washing process on chlorides removal and control

According to compositions analyzed above and the potential factors which affected chlorides removal and control, Orthogonal Test of $L_{16}(4^5)$ which was listed in Table 2 was prepared to investigate relatively optimum process conditions. Program and results for Orthogonal Test of $L_{16}(4^5)$ was shown in Table 3. Removal rate of soluble solids and chlorine were acted as indicators of the experiments of multi-step water-washing process. But the removal rate of soluble solids (F_1) was a contrary indicator while the other (F_2) was a positive indicator. And one thing to be noted is that the F_1 was calculated on the basis of dried filtration cake while the F_2 was determined on the basis of the accumulative amount of chlorine in the filtrates. So a correction method was introduced to balance the two indicators by replacing the original contrary indicator F_1 with the value of one minus soluble solids removal rate which was defined as f_1. And comprehensive results (F) were calculated according to the following formula:

$$F = f_1 \times 0.4 + F_2 \times 0.6 \tag{1}$$

Table 2. The levels and factors of orthogonal experiment.

Level	L(mg/L)	T(℃)	W(min)	V(r/min)	D(per)
1	3	30	3	50	1
2	6	40	10	80	2
3	10	50	30	100	3
4	20	60	60	150	4

Table 3. The $L_{16}(4^5)$ orthogonal experiment table.

Test	L(mg/L)	T(℃)	W(min)	V(r/min)	D(per)	Results		F(%)
						f_1(%)	F_2(%)	
1	1	1	1	1	1	0.8044	0.8694	0.8434
2	1	2	2	2	2	0.7758	0.8920	0.8455
3	1	3	3	3	3	0.5713	0.9171	0.7788
4	1	4	4	4	4	0.4667	0.9658	0.7662
5	2	1	2	3	4	0.6870	0.9627	0.8524

6	2	2	1	4	3	0.7150	0.9281	0.8428
7	2	3	4	1	2	0.7129	0.9709	0.8677
8	2	4	3	2	1	0.7725	0.9141	0.8575
9	3	1	3	4	2	0.6202	0.9115	0.7950
10	3	2	4	3	1	0.5901	0.9144	0.7847
11	3	3	1	2	4	0.2082	0.9245	0.6380
12	3	4	2	1	3	0.7994	0.9080	0.8646
13	4	1	4	2	3	0.4348	0.9647	0.7527
14	4	2	3	1	4	0.3410	0.9806	0.7247
15	4	3	2	4	1	0.3584	0.9500	0.7133
16	4	4	1	3	2	0.4982	0.9772	0.7856
Range	0.111	0.069	0.042	0.052	0.078			

According to the experimental results shown in Table 3, visual analysis indicated that result of Test 7 was more significant than other results which meant that parameters of Test 7 were relatively appropriate. It's obtained from ranges of the factors that the primary relation of five influential factors is: L＞D＞T＞V＞W. Based on the theoretic analysis, chlorides like NaCl, KCl and $CaCl_2$ present excellent solubility in water. The tendency of the solubility of compounds also indicated that solubility of chlorides like NaCl and KCl changed little while that of calcium chloride increased when temperature was raised. What's more, solubility of calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$) formed by calcium oxide (CaO) decreased significantly along with the rise of temperature. Combined with actual operation during laboratory experiments, most amounts of soluble solids dissolved into solution in 10 minutes and when washing time was longer than 10 minutes, total growth was less than 8%. So the relatively optimal and optimized parameters was determined that 6mL/g, 50℃, 10 minutes, 50 r/min and two. The corresponding trend charts for experiments of optimizing washing time was shown in Fig. 2.

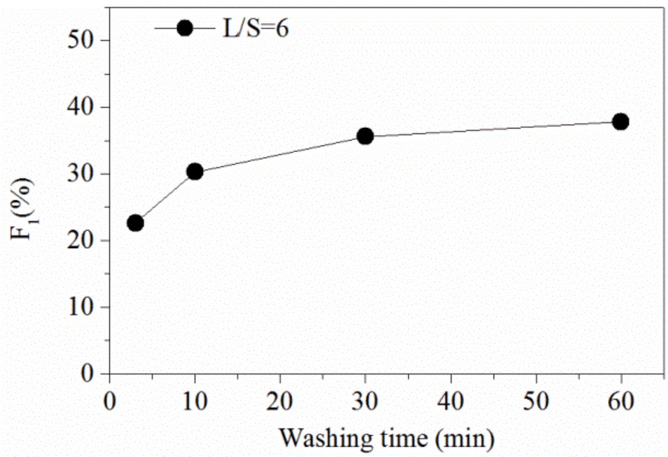

Fig. 2. Trend chart for experiments of optimizing washing time

3.3. Effects of cyclic water-washing process on chlorides removal and control

Apparently, it's not a wise way in which much wastewater generated to remove and control chlorides in MSWI fly ash with the method of conducting washing process with deionized water continuously under the optimal experimental parameters. Considering the great solubility of chlorides in water, cyclic water-washing process was carried out to recycle the solution of water. Total removal rate of soluble solids and chlorine at the end of each batch during process of the cyclic water-washing was shown in Fig. 3.

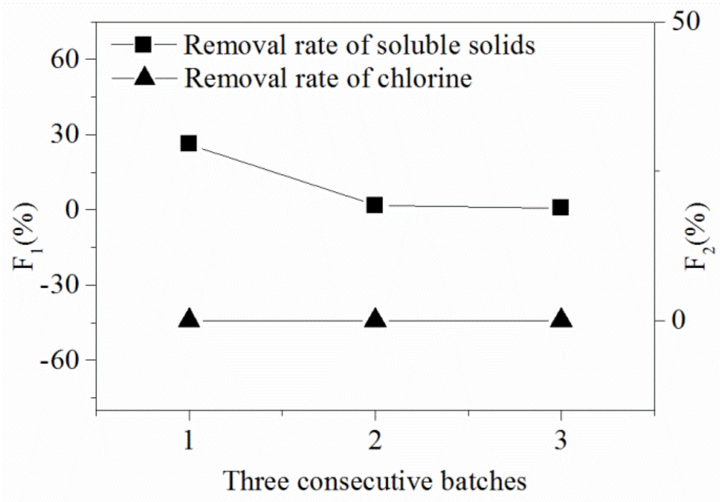

Fig. 3. Total removal rate of soluble solids and chlorine at the end of each batch during process of the cyclic water-washing

As shown in Fig. 3, the removal rate of soluble solids was below 27% and even was nearly zero while that of chlorine was approximately zero at the end of each batch. More specifically, with the cycle continuing, the water for washing got to be high alkaline and contained high concentration of calcium which reduced the solubility of components such as calcium carbonate and calcium hydroxide because of the ionic equilibrium of calcium. On the other side, only a part of wastewater was discharged when the cycle ended and certain amount of fresh deionized water was added into the remained water to conduct the subsequent cyclic water-washing experiments. The discharged wastewater could also be reused through concentrating by evaporation.

3.4. Effects of calcium hydroxide on chlorides removal and control

Calcium hydroxide is a cheap and strong alkaline chemical which could be added into the solution to affect the ionic equilibrium and solubility equilibrium associated with calcium. The trend chart of removal rate of soluble solids and chlorine for employing two different extracting agents was shown in Table 4.

Table 4. Comparison between F_1 and F_2 when saturated calcium hydroxide solution was added.

Number	Leaching agent	F_1(%)	F_2(%)
1	Deionized water	30.52	96.27
2	Saturated calcium hydroxide solution	25.52	91.15

According to the results presented in Table 4, both the removal rate of soluble solids and that of chlorine was lower when the extracting agent was saturated calcium hydroxide solution. Possibly, calcium hydroxide added into the solution affected the equilibrium of calcium chloride and calcium hydroxide during the washing process which shifted the solubility equilibrium to left. What's more, removal rate of soluble solids decreased by 16.38% while that of chlorine decreased by 10.5%. It indicated that removal amount of soluble solids could be controlled by adding calcium hydroxide.

4. Conclusions

Multi-step and cyclic water-washing processes were applied to remove and control chlorides from MSWI fly ash to facilitate the further reuse as basis with cement kiln. In order to meet requirements for raw materials in cement kilns for silicon and calcium, calcium hydroxide was add to replace the pure deionized water to stop the calcium compounds from being washed away too much, though the removal rate of chlorine decreased a little.

Cyclic water-washing experiments indicate that under the optimal parameters of multi washing, the removal rate of chlorine was beyond 99% while removal rate of soluble solids was controlled below 27% at the end of each batch. What's more, the discharged wastewater could also be reused through concentrating by evaporation especially if this technology was applied to industrialized mass production.

This research identified that measures like water-washing could be taken to easily remove and control chlorides from MSWI fly ash. Compare the analysis of experimental results with theoretic analysis, they are agreement, which proving the efficiency of washing mechanisms for chlorides removal and control.

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